Investigation of Ionic Liquid as Hydrate Inhibitor at Different Range of Temperature and Pressure

by

Muhammad Zulqarnain bin Hatta
13757

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Petroleum Engineering)

MAY 2014

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CERTIFICATION OF APPROVAL

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Approved by,

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(A.P. Dr Ismail bin Saaid)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
MAY 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

_____

MUHAMMAD ZULQARNAIN BIN HATTA

ABSTRACT

Hydrate is an ice-like structure which is formed by the interaction between water molecules and natural gas at high pressure and relatively low temperature. Methane hydrate deposit is identified at deepwater marine settings and permafrost settings [1]. In this project, the equilibrium phase of methane hydrate is measured in the presence of ionic liquid as hydrate inhibitor. Ionic liquid is chosen due to its dual function inhibitors which can give thermodynamic and kinetic inhibition effects. In contrast to conventional thermodynamic inhibitor such as methanol and ethanol, ionic liquid is needed in a low dosage and it is environment friendly solvents [2]. The performance of this ionic liquid towards the equilibrium phase boundary of methane hydrate is studied using the hydrates studies system (HYDREVAL). From the literature research studied, 1 wt% of 1-butyl-3-methyl-imidazolium bromide ([BMIM]-Br) is used as ionic liquid and several runs are conducted at pressure range of 3 - 6 Mpa to investigate the performance of [BMIM]-Br at different pressure and temperature. The equilibrium phase of methane hydrate in the presence of [BMIM]-Br is compared with other hydrate inhibitors from previous studies likes methanol and [EMIM]-Cl. In the presence of [BMIM]-Br, there is a temperature shift on the equilibrium phase of methane hydrate. Compare to conventional thermodynamic hydrate inhibitor, methanol shows a significant temperature shift. However, high dosage of methanol is needed to give a significant thermodynamic effect.

ACKNOWLEDGEMENT

Praise to God that in His will and strength given, I managed to complete this Final Year Project which has proved to be really beneficial to me. My deepest appreciation is towards my supervisor, A.P. Dr Ismail bin Saaid for his informative supervision, advice, guidance and countless hours spent in sharing his knowledge.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In the recent years, oil and gas industry is moving towards deepwater exploration to search for alternative hydrocarbons sources where hydrates deposits are favorable. Gas hydrates reserves have been found as potential resources. Hydrates deposits have also been discovered around the world under the deep ocean floor and permafrost environment. Some countries including United States and Japan have now been looking forward to develop gas hydrates as an energy sources. United States Congress is currently examining the hydrate beds in the Alaskan North Slope and the Gulf of Mexico [8].

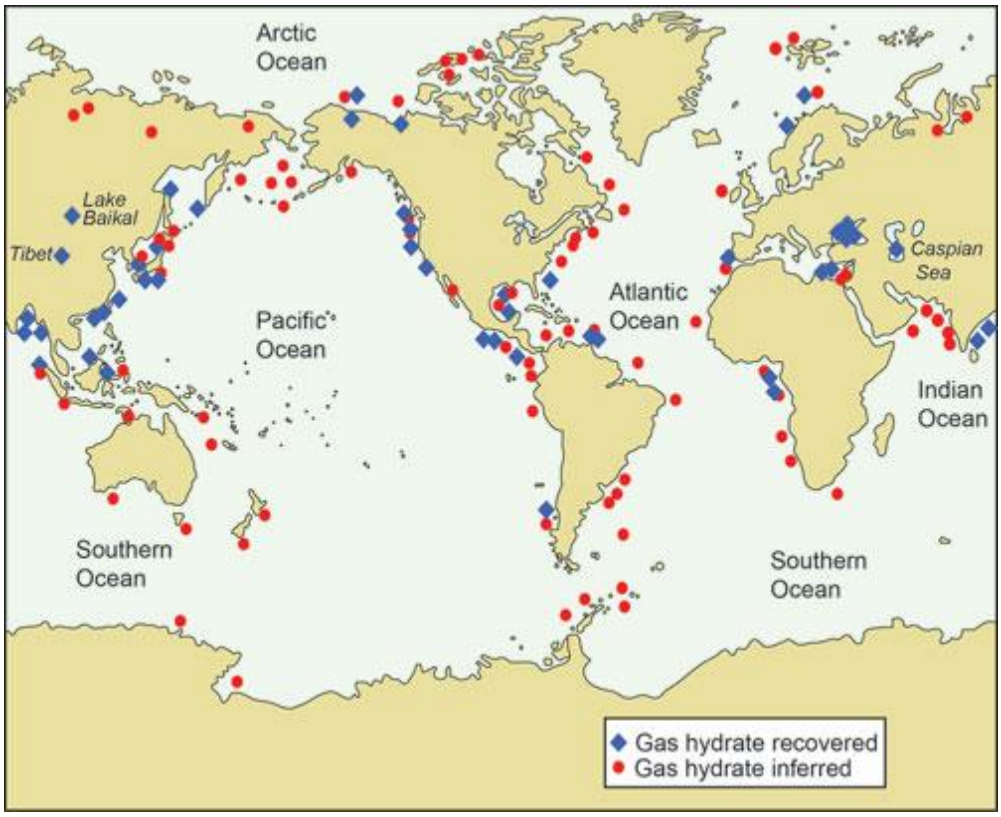


Figure 1**:** Gas hydrate occurrence in the world [5]

Figure 1 shows that gas hydrate has been discovered worldwide yet there are still a lot places to be recovered. The red dots represent the known location for gas hydrates occurrence while the blue dots represent the inferred gas hydrates occurrence. The occurrence of gas hydrates is seen in many continental margin settings and in onshore of offshore permafrost [4].

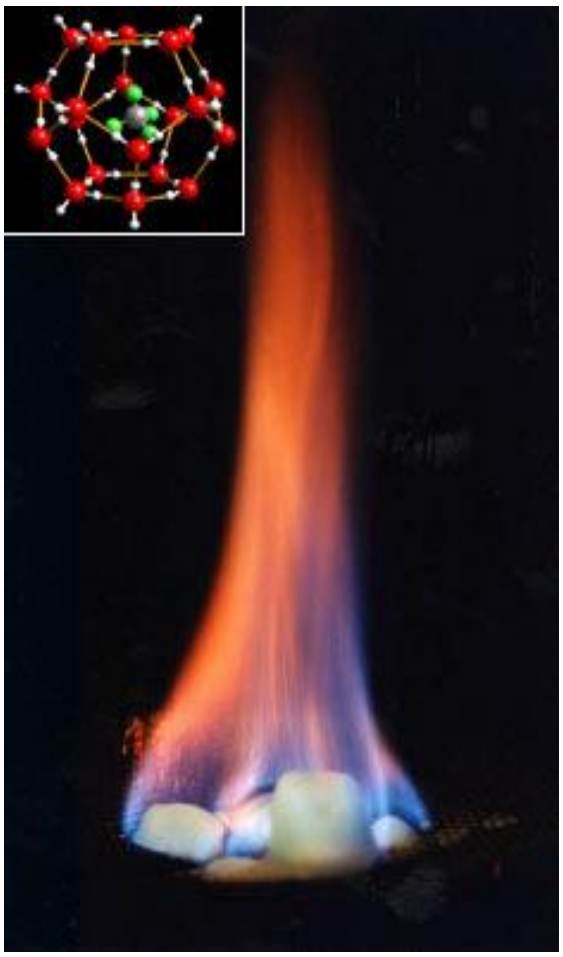


Figure 2: Clathrate Structure [4]

Gas hydrate is a solid ice-like structure formed from the mixture of water molecules with gaseous molecules at high pressure and relatively low temperature conditions. Figure 2 shows the clathrate structure. Water molecules (red molecules) act as cage which surrounded the lighter hydrocarbons and gaseous components (green molecules). Some of the natural gases that can form gas hydrate include methane, ethane, propane and carbon dioxide. Methane hydrate is one of the gas hydrates formed from the combination of methane (CH_4) molecules trapped inside the lattice structure of water molecules. There is

no occurrence of hydrogen bonding between the methane and water molecules [8]. Thus, methane hydrate can be called as methane clathrates.

A lot of research have been done to study the characteristics of gas hydrates and to find the best method to extract gas hydrate [8][12]. If extracted, gas hydrate can provide energy sources as an alternative crude oil. At standard condition, a cubic meter of methane hydrate consists of about 160 cubic meter of methane gas [1]. The common extraction technology includes thermal stimulation, depressurization and inhibitor injection [8]. Thermal stimulation and depressurization have been conducted to produce natural gas from gas hydrate while inhibitor injection is still under laboratory condition. In 2007, thermal injection and depressurization test have been conducted at the Malik permafrost well [12]. However, inhibitor injection is still under experimental stage. Currently, ongoing research on inhibitor injection is done to investigate the effectiveness of different types of hydrate inhibitors. Some of the inhibitors that are tested include 1-ethyl-3-methylimidazolium chloride (EMIM-Cl) with the conventional inhibitors such as monoethylene glycol (MEG) and sodium chloride (NaCl).

The common application of hydrate inhibitor is also applied in flow assurance to remove gas hydrate blockage which will improve oil transportation through pipeline. Normally, pipeline or tanker truck is used for the transportation of natural gas. This gas is transported in the liquid form which is called as Liquefied Natural Gas (LNG). Blockage caused by the hydrate inside the gas pipeline can reduce the production of the gas and potential explosions which may occur. In order to improve the flow, mitigation needs to be done to remove gas hydrate blockage.

There are not much applications of hydrate inhibitor used for methane hydrate production from natural hydrate deposits in the reservoir. Thus, this research is emphasized on **the production of methane gas from hydrate deposits** since methane hydrate is acknowledged as unconventional hydrocarbon [1].

1.2 PROBLEM STATEMENT

There are several factors that lead to the study of hydrate inhibitor towards the phase equilibrium of gas hydrate. As mentioned earlier, the application of hydrate inhibitor is currently focusing on the removing of hydrates inside the pipeline since hydrate affect the flow assurance. Hence, potential explosion may occur because the integrity of the pipeline is affected. In order to remove the hydrate blockage inside the pipeline, conventional hydrate inhibitor is used to dissociate the gas hydrate structure. In other words, the gas hydrate structure is disturbed in the presence of hydrate inhibitor. However, the **study of hydrate inhibitor for the extraction of gas hydrate is still ongoing** [1]. Thus, the application of hydrate inhibitor can be one of the potential methods to be applied in the production of gas from hydrates deposits.

Nowadays, **oil reserve starts to deplete** while oil and gas companies are now moving towards the deepwater exploration where gas hydrates occurrence is favorable. "Methane hydrates contained a highly concentrated form of methane, with a cubic meter of idealized methane hydrate contained 0.8 m^3 of water and more than 160 m^3 of methane at standard temperature-pressure conditions" [1]. Besides, the heat content of methane has about 80% of crude oil which makes methane a good fuel source [3]. Thus, gas hydrates has the potential to be the alternative energy for the crude oil as well as unconventional hydrocarbons. Although there are several extraction methods being applied such as thermal stimulation, depressurization and inhibitor injection, yet the most suitable extraction of gas hydrate is still to be studied [12]. From the past research, **thermal stimulation and depressurization methods have some drawbacks** which initiate the study of inhibitor injection [8].

The conventional hydrate inhibitor like methanol, monoethylene glycol (MEG), and diethylene glycol (DEG) is known as **high dosage hydrate inhibitor (HDHI). In simple words, conventional hydrate inhibitor is needed in large amount and harmful if released to the environment**. There are two types of hydrate inhibitor which are thermodynamic inhibitor and kinetic inhibitor. Thermodynamic inhibitor shifts the equilibrium temperature of hydrate to a lower temperature whereby kinetic inhibitor delays the formation of hydrate.

Conventional hydrate inhibitor is categorized under thermodynamic inhibitor. The use of kinetic inhibitor is still new and it is known as low dosage hydrate inhibitor (LDHI). Further explanation on the types of hydrate inhibitor is discussed on Chapter 2.

1.3 OBJECTIVES

The purpose of this project is to study the equilibrium phase boundary of methane hydrate in the presence of ionic liquids thermodynamically. The aims of this project are as follows:

1) To investigate the ionic liquid as hydrate inhibitor at different range of pressure and temperature.
2) To determine the thermodynamic inhibition effect of ionic liquid as hydrate inhibitor.
3) To compare the effectiveness of BMIM-Br with other hydrate inhibitor from previous study.

1.4 SCOPE OF STUDY

This research focused on the **methane hydrate extraction** as the unconventional hydrocarbons. Thorough **literature research is done** to get some ideas on the hydrate occurrence and previous researches that are relevant towards this study are analyzed. Deepwater environment is studied due to the methane hydrate occurrence in Malaysia. From all the three methods available for the extraction of gas hydrates, the author focused on the **inhibitor injection** and its applications. The **equilibrium phase of methane hydrate** is studied in the presence of ionic liquid through laboratory investigation. The ionic liquid used in this research is **[BMIM]-Br**. The equipment used to study the phase equilibrium of the formation and dissociation of methane hydrate is **hydrate studies system (HYDREVAL).**

1.5 RELEVANCY AND FEASIBILITY OF PROJECT

Currently, the gas hydrates occurrence has been discovered worldwide yet to be discovered. This study is an important research on the extraction of methane hydrate with the application of inhibitor injection. Furthermore, gas hydrates is discovered at Gumusut-Kakap field in Malaysia [20]. The inhibitor injection methods may be applied in this field for the production of methane hydrate. Besides, the application of ionic liquid as hydrate inhibitor can be further studied as it is acknowledge as low dosage hydrate inhibitor (LDHI). This project is expected to be completed and achieved its objectives within the time frame given.

CHAPTER 2

LITERATURE REVIEW

2.1 METHANE HYDRATE

Methane hydrates is a crystalline solid which is the combination of molecular methane (CH_4) inside the lattice structure formed by water molecules. Methane is called as guest a molecule which is surrounded by water molecules. Besides, there are no actually hydrogen bonding occurs between the methane and water molecules [8]. The figure 3 illustrates the model of methane hydrates. From the model, a methane molecule is surrounded by cage-like formed by water molecules.

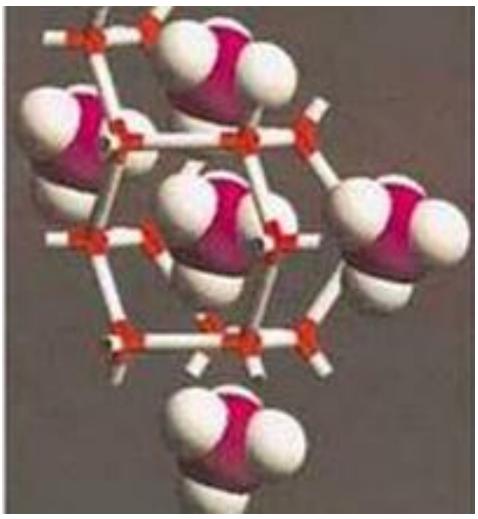


Figure 3: A structure of methane hydrate [3]

There are four factors that cause the formation of methane hydrates. These include the presence of gas molecules (methane), water molecules, high pressure condition and low temperature condition. In the ocean environment, ice crystals starts to form into crystal structure when methane is saturated with water [8].

Figure 4 shows the phase diagram of methane hydrate in deepwater marine setting and permafrost which indicated where methane hydrate is stable. For marine cases, gas hydrate is stable at water depth of 1200 m while in permafrost cases, methane hydrate is seen stable at water 200 m and above. Hydrate stability zone for marine cases is much smaller compare to permafrost cases.

The temperature of gas hydrate stability zone at deepwater marine settings ranging from 0 °C to 17 °C whereby in permafrost settings the temperature of methane hydrate stability zone ranging from -20 °C to 15 °C. In this research, the main interest is on the phase boundary of deepwater marine settings. **In order to produce methane gas from methane hydrate deposit at this environment, the phase boundary of methane hydrate need to be shifted to a lower temperature.** Hence, a larger hydrate free zone can be achieved.

Methane hydrate can only be found in specific zone where the pressure and temperature conditions are well known. Outside the stability zone, methane hydrate exists as free gas or gas dissolved in pore waters at pressure-temperature conditions and estimated 99% of gas hydrate is formed in ocean sediments [1].

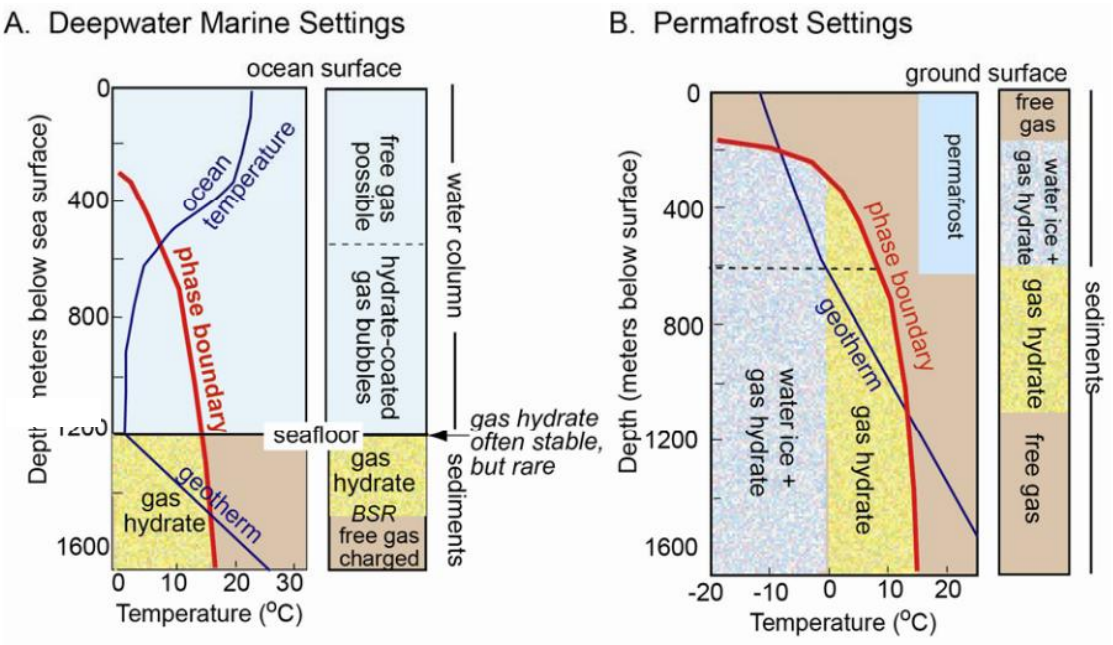


Figure 4: Phase diagram of methane hydrate in (A) deepwater marine settings and (B) permafrost [1]

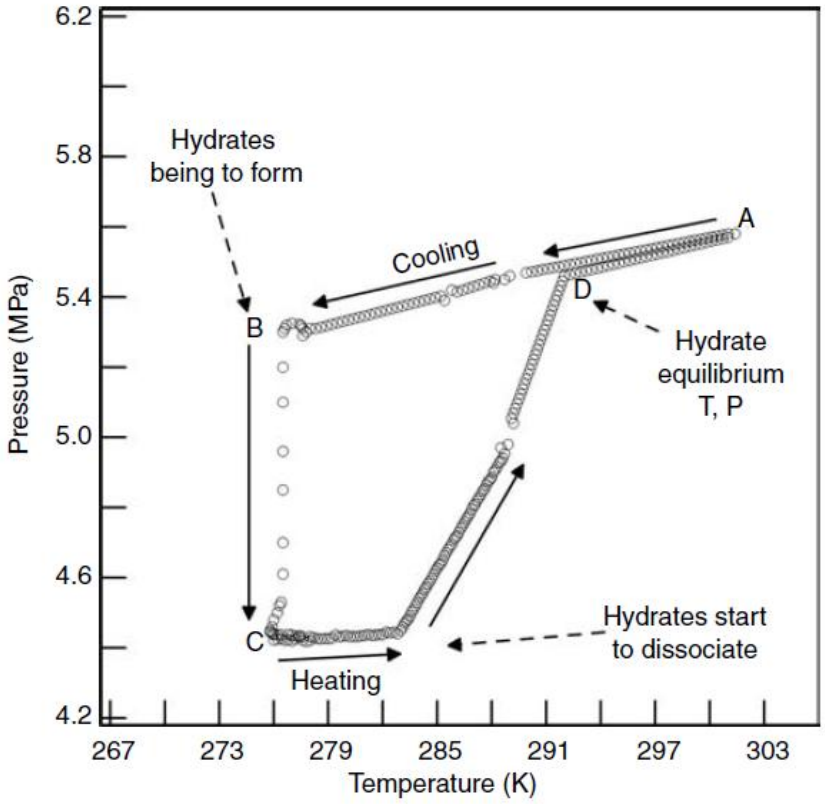


Figure 5: Temperature and pressure trace for formation of simple methane hydrates [18]

Figure 5 shows the temperature and pressure trace for formation of simple methane hydrate from HYDREVAL [18]. During the cooling process from point A to B the hydrates start to form and when the hydrate is fully formed, there is a sudden pressure drop (point B) due to the gas filling inside the hydrate former. Methane hydrate is fully formed when the methane gas filled the hydrate former and there is no pressure drop (point C). As the temperature increased from point C to point D, hydrates start to dissociate. Methane gas is released from the hydrate former at this point and the pressure started to build up. The equilibrium temperature and pressure is measured at point D where the intersection of hydrate formation line and dissociation line met.

2.2 EXTRACTION METHODS

As mentioned in Chapter 1, oil and gas industry is moving towards deepwater exploration where the hydrate occurrence is favorable. Methane gas is a good fuel source as its contain 80 % of heat content of crude oil [8]. The gathering and transportation of methane hydrate are not practical and not economic as methane hydrates is in solid structure. A lot of problems are occurred if hydrates formed inside the gas pipeline. Several methods have been studied and practices to extract methane from hydrate formation. The idea of extraction of gas hydrate is to disturb the factors that initiate the formation of hydrate. Currently, there are three methods for the extraction of gas hydrates which include thermal stimulation, depressurization and inhibitor injection.

The common extraction technique of methane hydrates is by thermal stimulation. In this technique, steam or hot fluids is pumped down into the hydrate layers to partially melt the hydrate beds. Thus, gas is produced through the borehole. This method can be very easy to perform but the heating fluids would be cost prohibitive. Besides, energy is consumed to heat the water to extract methane gas from hydrate formation. In other words, energy is used to produce energy. Figure 6 illustrates the three current extraction methods.

The second method to extract methane hydrate is depressurization. The idea of this method is that the free gas underlying the gas hydrate will be extracted first. This will cause the pressure of upper sediment to decrease and lead to gas dissociation [3]. This method has some disadvantages since rapid depressurization can cool the sediments and affected the machinery. Moreover, there is some limitation to be met to conduct this method. Free gas layer underlying gas hydrate formation need to be met first before this method is chosen because the bottom layer of gas hydrate is drilled to reduce the pressure inside the reservoir.

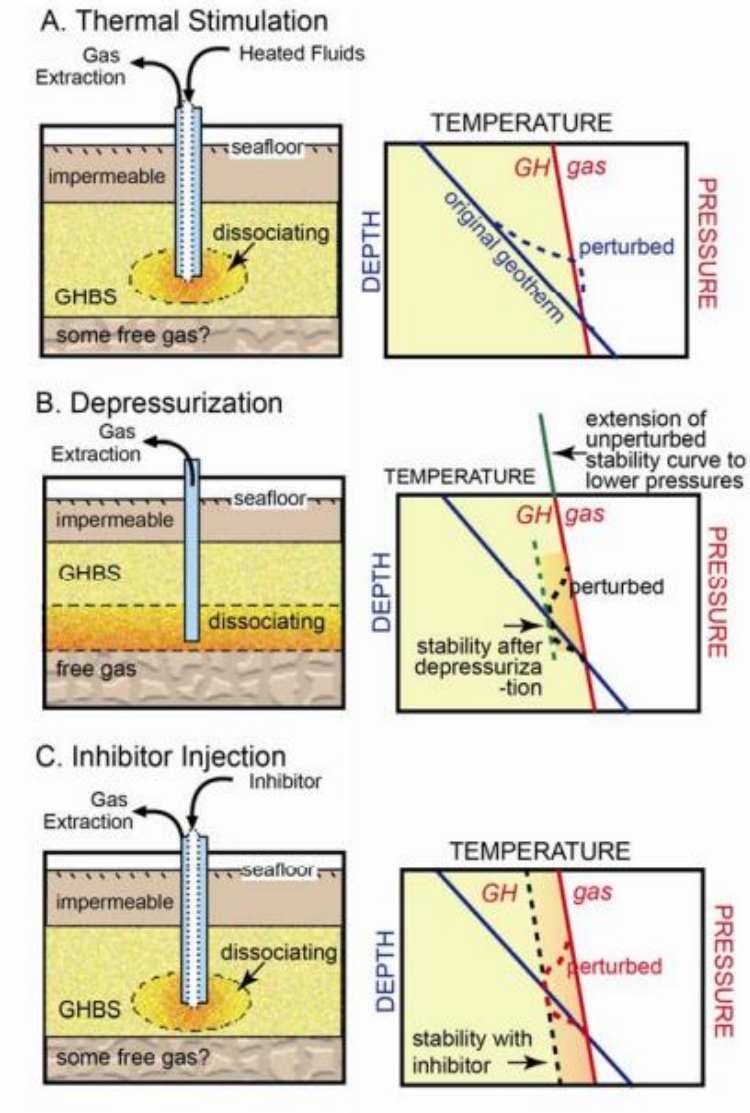


Figure 6: Possible methods for producing gas from gas hydrate deposit are thermal stimulation (A), depressurization (B) and inhibitor injection (C) [1]

Inhibitor injection is seemed to be a good technique for the extraction of gas hydrates. The conventional hydrate inhibitors such as methanol, ethanol and glycol are injected into the sediment beds at a given pressure to reduce the formation temperature of hydrates which lead to dissociation. Different amount and composition of inhibitors have different effectiveness on the dissociation of methane hydrates [3]. **The problem with the conventional hydrate inhibitor is that this inhibitor is needed in large dosage.** Besides, this type of hydrate inhibitor is harmful to the environment.

2.3 IONIC LIQUID

One of the extraction methods mentioned above is inhibitor injection where a chemical which acts as inhibitor is injected to dissociate the hydrate crystals. Inhibitor is used to alter the gas composition so that the hydrate formation temperature reduced and hydrate formation can be delayed. Currently, there are two types of hydrate inhibitor which are kinetic and thermodynamic inhibitors [11]. The most common thermodynamic inhibitors are methanol, mono-ethylene glycol (MEG) and glycol. These types of inhibitors are actually not preferable as it can affect the environment by releasing greenhouse gas. Thermodynamic inhibitors work by changing the hydrate dissociation by lowering the dissociation temperatures while kinetics inhibitors work by slowing down the formation or nucleation of hydrates [14]. Kinetic inhibitor is also known as low dosage hydrate inhibitor (LDHI).

Ionic liquid is type of salt with a melting point below some arbitrary temperature. There are many applications of ionic liquids such as solvents, stoichiometric organic synthesis and catalyzed reactions [22]. It comprises of organic anions or inorganic anions and organic cations [19]. There are two types of ionic liquids which are hydrophobic ionic liquids and hydrophilic ionic liquids. The ionic liquid used in this research ([BMIM]-Br) is categorized as hydrophilic ionic liquid [19].

A lot of studies were done on the performances of ionic liquids as dual function inhibitors. Ionic liquids can actually act as thermodynamic and kinetic inhibitors. From the previous study, it is proven that ionic liquids can shift the dissociation temperature and slow down the nucleation of methane hydrate [15]. The induction time of methane hydrate formation of individual ionic liquids is compare to see the kinetic inhibition effect. Besides, the temperature shift of individual ionic liquids is studied which reflects the thermodynamic effects.

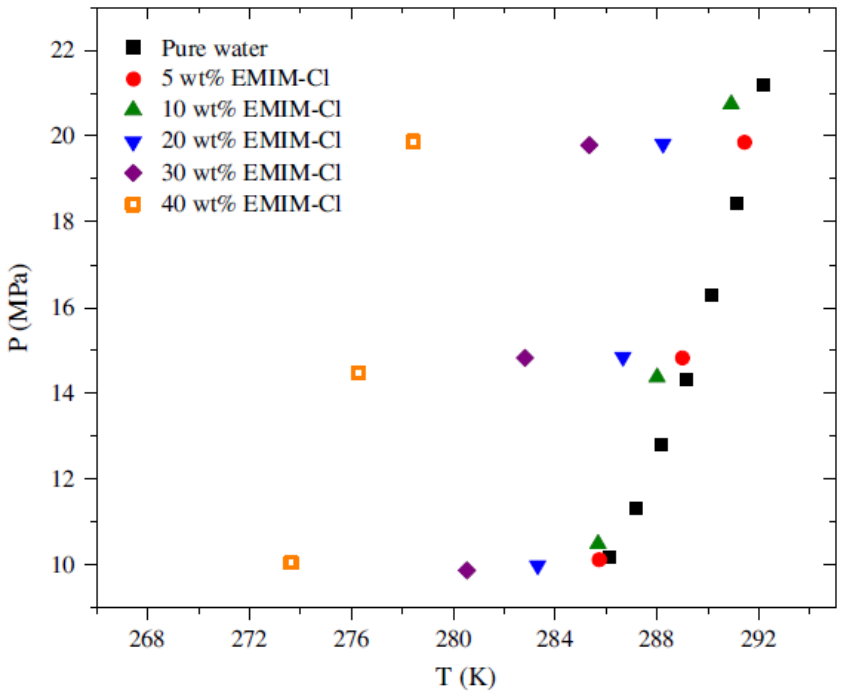


Figure 7: The effect of concentration of ionic liquid towards the dissociation curve [11]

One of the ionic liquid capabilities is to act as thermodynamic inhibitor. Ionic liquid is able to shift the equilibrium temperature of methane hydrate to a lower temperature hence promote the hydrate free zone. Studies on the effect of the concentration of ionic liquid towards the dissociation curve are shown in figure 7. In this study the performance of ionic liquids and their mixtures in inhibiting methane hydrate formation is investigated [11]. The ionic liquid tested in this research is 1-ethyl-3-methylimidazolium chloride ([EMIM]-Cl). Different concentration of ionic liquid is studied and the dissociation curve is plotted. From the research, higher concentration of [EMIM]-Cl shows a significant temperature shift compare to smaller concentration. The sample with 40 wt% of [EMIM]-Cl shifted the methane hydrate dissociation curve to a much lower temperature compare to sample with 5 wt% of [EMIM]-Cl.

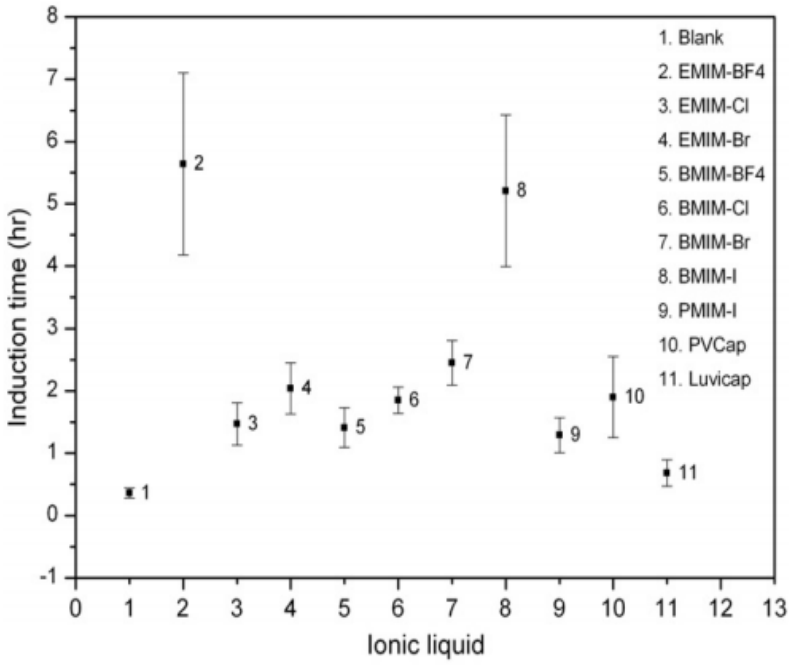


Figure 8: The induction time of methane hydrate formation from blank samples and samples containing different inhibitors [14]

Ionic liquid can also acts as kinetic inhibitor where it delays the formation of hydrate. This kinetic performance of ionic liquid is studied in several articles. The common equipment used to study the dual function of inhibitors characteristics of ionic liquids is using the high-pressure micro-differential scanning calorimeter (μDSC). Figure 8 shows the induction time of methane hydrate formation in the presence of different inhibitors [14]. The induction time is the time taken for the hydrate to form. In the presence of ionic liquids the formation of methane hydrate is delayed. From the above figure, [EMIM]- BF_4 have the longest induction time compare to others whereby blank samples gives the shortest induction time. This proved that ionic liquids can also act as kinetic inhibitor as well as thermodynamic inhibitor.

CHAPTER 3

METHODOLOGY

3.1 RESEARCH METHODOLOGY

Before executing the project, a thorough research was conducted to expose self to the knowledge of hydrate and ionic liquid as hydrate inhibitors. During the research methodology, numbers of research papers which are relevant to the topics are being studied to get some ideas regarding the project. Figure 9 shows the flow of the research methodology.

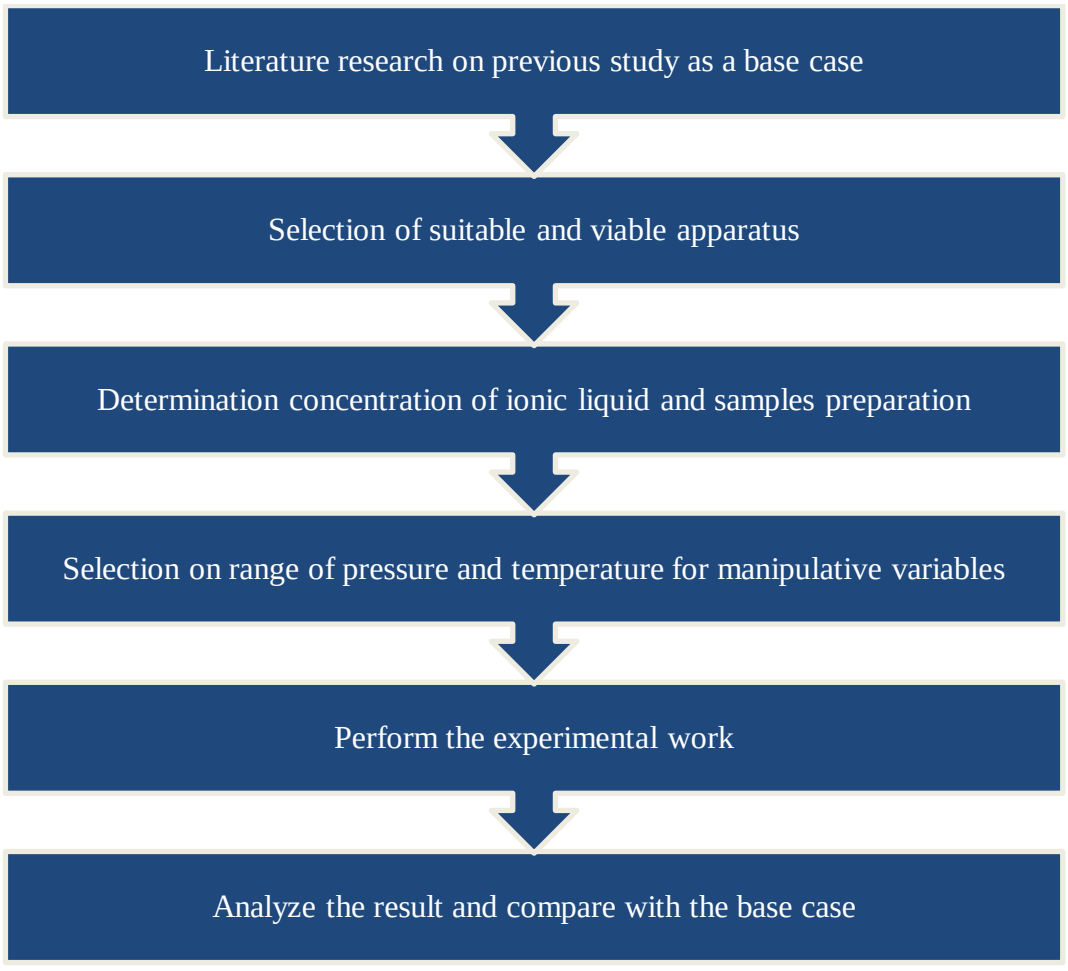


Figure 9: Research methodology flow

3.2 EXPERIMENTAL METHODOLOGY

3.2.1 Apparatus

For the experimental work, **hydrates studies system (HYDREVAL)** was used to study the phase equilibrium of hydrate formation and dissociation as well as the effect of hydrate inhibitor. It is a motor driven PVT cell which provides four methods consist of isochoric (constant volume), isobaric (constant pressure), isothermal and visual method. Figure 10 shows the schematic of HYDREVAL equipment. The main components inside this equipment include sapphire cell, magnetic stirrer and piston. All of the liquid and gas are injected to the sapphire cell by using the external pump. The magnetic stirrer was used to make sure the sample is mixed with methane gas throughout the experiment. HYDREVAL software was used to regulate all the parameters which include pressure, temperature and control volume. Table 1 shows the features of HYDREVAL equipment.

Table 1: Features of HYDREVAL equipment [21]

Features	**Remarks**
Pressure	: 200 Bar
Temperature	: -20 °C to 150 °C
Temperature regulation	: ± 0.1 °C
Cell volume	: 80 cm^3
Volume accuracy	: 0.01 ml
Pressure accuracy	: 0.1 % Full scale
Temperature accuracy	: 0.1 °C
Stirring mechanism	: Magnetic drive

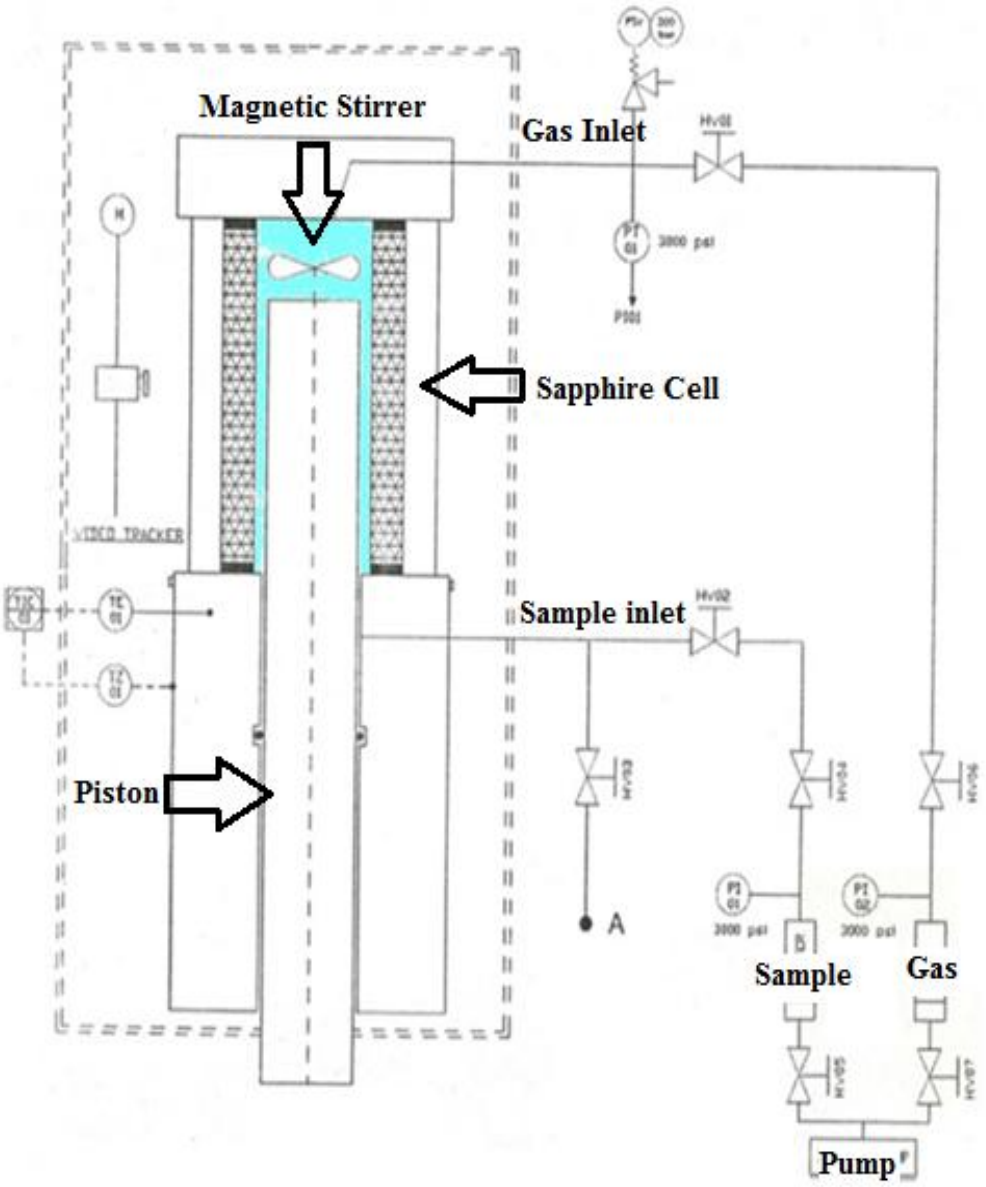
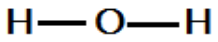
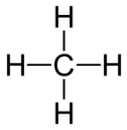
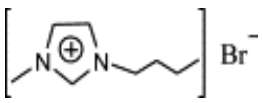


Figure 10: Schematic diagram of HYDREVAL [16]

3.2.2 Materials

Materials used for the experiment are distilled water (H_2O), methane gas (CH_4) and 1-butyl-3-methylimidazolium bromide ([BMIM]-Br). Table 2 shows the detail description of the components used in the project.

Table 2: Detail description of the materials

Symbol	Component name	Chemical structure	Purity/supplier
H_2O	Water		UTP
CH_4	Methane		98 % UTP
[BMIM]-Br	1-butyl-3-methylimidazolium bromide		97 % Irama Canggih

3.2.3 Preparation of Sample

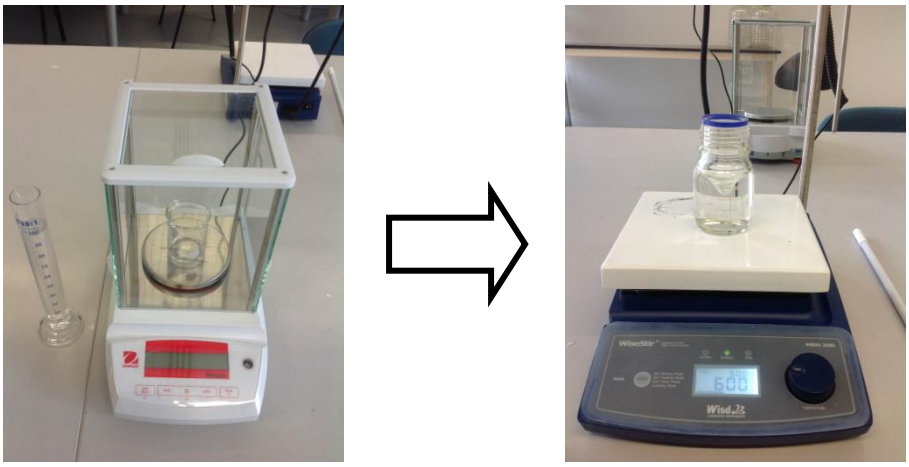
Due to the time constraint, only one concentration of the sample was tested. **The concentration of the sample used for this experiment is 1 wt%.** The sample was prepared using below equation.

$$\text{Mass percent (wt\%)} = \frac{\text{mass of solute powder (g)}}{\text{mass of solution (g)}} \text{ x } 100\ \%$$

The mass of the sample needed is 100 g. The mass of solute powder was calculated using the above equation. The sample was prepared at room temperature of 25 °C. During the mixing process, ionic liquid powder was slowly added into the beaker and the sample was stirred using the magnetic stirrer at 600 rpm for about 1 to 2 minutes to make sure that the ionic liquid powder dissolved completely in the distilled water. Figure 11 shows the flow of the preparation sample while table 3 shows the calculation for the sample preparation.

Table 3: Calculation to prepare 1 wt% of [BMIM]-Br

$\text{Mass percent (wt\%)} = \frac{\text{mass of solute powder (g)}}{\text{mass of solution (g)}} \text{ x } 100$	
Mass of solute	1 g
Mass of distilled water	100 g – 1 g = 99 g



1. Weigh the ionic liquid powder 2. Mixing process

Figure 11: Sample preparation flow

3.2.4 Measurement of Hydrate Equilibrium Point

The equilibrium points of hydrate formation were measured using **isochoric method (constant volume).** The sapphire cell was washed using distilled water and then vacuumed alternately for two rounds. Afterwards, the cell was flushed with methane gas to ensure it was air free for about half an hour. 25 cm^3 of sample with desired concentration and 55 cm^3 of methane gas was injected into sapphire cell using external pump in separate line. Then, the temperature was cooled down to 2-3 °C above hydrate equilibrium. The methane gas was then supplied into the cell until the desired pressure is achieved. Table 4 shows the sample concentration and pressure condition for this experiment.

Table 4: Sample concentration and pressure condition

Sample concentration	1 wt% of [BMIM]-Br
Pressure condition	30 Bar and 60 Bar

After the stabilized pressure was achieved, the experiment was run. To remove the clathrate hydrate from gas-liquid interface, stirrer speed of 504 rpm was chosen. The hydrate formation in the vessel was detected through visual observation and every data was recorded for each reduced temperatures. The temperature was increased slowly for hydrate dissociation. As a result, a pressure-temperature diagram was obtained for each experiment conducted.

3.3 PROJECT ACTIVITIES

3.3.1 Gantt Chart

		FYP I							FYP 2						
No	Activities	1-2	3-4	5-6	7-8	9-10	11-12	13-14	15-16	17-18	19-20	21-22	23-24	25-26	27-28
1	Project title selection	■													
2	Preliminary research work		■	■											
3	Extended Proposal submission			●											
4	Proposal Defense				●										
5	Research work on materials and equipment					■	■	■							
6	Interim Report submission							●							
7	Sample purchasing and preparation								■	■	■				
8	Progress Report submission											●			
9	Experimental work											■	■	■	■
10	Pre-SEDEX												●		
11	Draft Report submission												●		
12	Dissertation and Technical Paper submission													●	
13	Viva														●

3.3.2 Key milestone

Table 5: Key milestone

Detail	Week
Topic Selection and Literature Research	FYP 1
Submission of Extended Proposal	FYP 1
Proposal Defense	FYP 1
Submission of Interim Report	FYP 1
Verification of Available Equipment	Week 2 - 5
Identification of the Experimental Procedures	Week 5
Laboratory Investigation	Week 6 - 11
Discussion on the Achieved Result	Week 11
Comparison with the Base Case	Week 12

CHAPTER 4

RESULTS AND DISCUSSION

4.1 EQUILIBRIUM MEASUREMENT OF METHANE HYDRATE

The experiment was conducted at two sets of different pressure of 30 Bar and 60 Bar. The temperature of pure methane was measured from the previous studies [18]. Table 6 and table 7 show the temperature of pure methane in the absence of ionic liquid. From this temperature, a set point of temperature can be made since the measured temperature is expected to shift the phase equilibrium of pure methane to a lower temperature.

4.1.1 Equilibrium temperature at 30 Bar.

Table 6 shows the experiment condition for sample at 30 Bar. At 30 Bar, the equilibrium temperature of pure methane was 1.52 °C. The result of sample at 30 Bar was shown in Figure 12. The equilibrium temperature of sample at 30 Bar was calculated from the pressure and temperature trace.

Table 6: Experiment condition at 30 Bar

Sample	Pressure (Bar)	Pure Methane Equilibrium Temperature (°C)
1 wt% of [BMIM]-Br	30	1.52

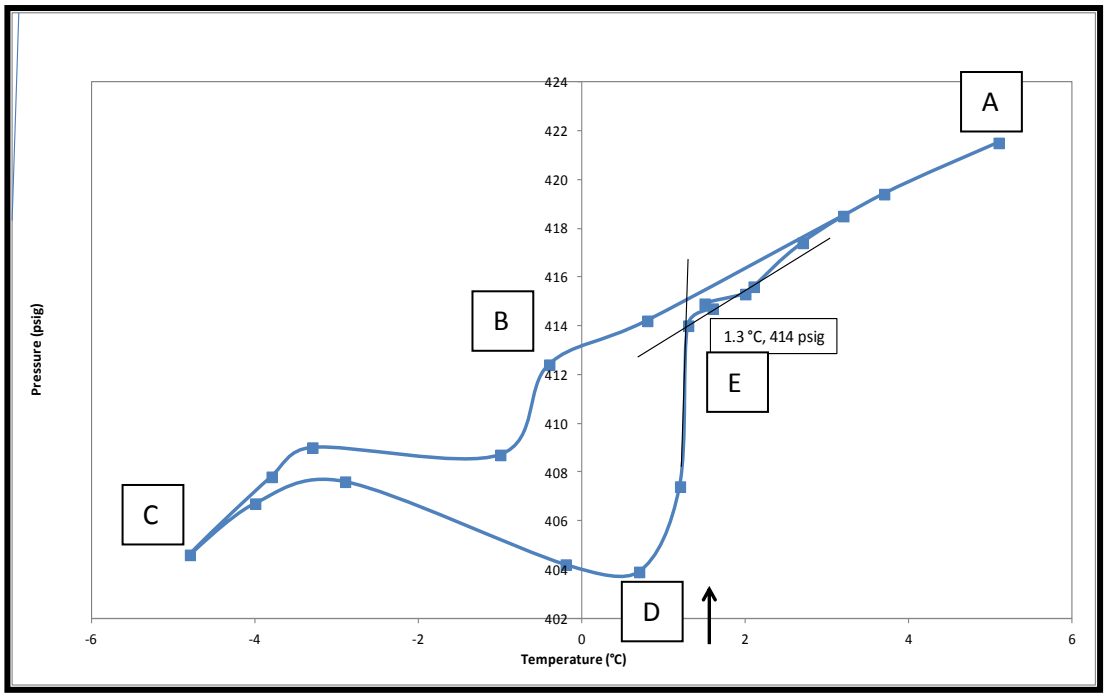


Figure 12: Pressure and temperature curve of methane hydrate at 30 Bar

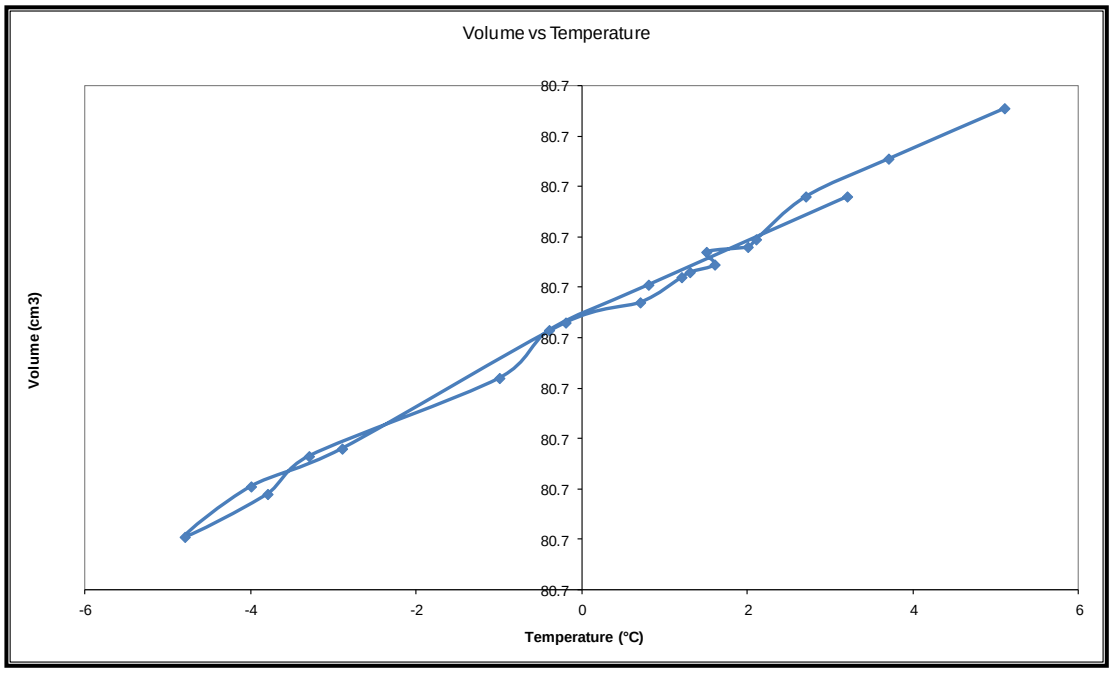


Figure 13: Volume and temperature curve at 30 Bar

Figure 12 shows the result of pressure and temperature curve of methane with 1 wt% of [BMIM]-Br. As the temperature of the cell decreased from A to B, the pressure was dropped due to the energy loss from the gas inside the cell (cooling process). Water molecule started to form ice as it reached the freezing point while methane gas started to react with water molecule. At point B, there was a sudden pressure drop since methane gas was contained by the ice structure as the hydrate growth had taken place. At point C, methane hydrate was fully formed. Thus, from point A to point C the formation of methane hydrate was observed.

When the heating process started at point C, methane hydrate started to dissociate as it reached the hydrate free zone. Pressure increased rapidly from point D to E reflecting the freed methane gas from the ice structure and methane hydrate started to dissociate. Line from point C to point D reflected the dissociation of the sample. **The intersection of two lines at point E shows the hydrate equilibrium temperature and pressure of the sample**. The equilibrium pressure was noted at 28.54 Bar and the equilibrium temperature was noted at 1.3 °C. At this point, methane hydrate has fully dissociated. Figure 13 shows the volume and temperature curves at 30 Bar. The volume was kept constant (isochoric) at about 80 cm^3. Table 7 summarizes the methane hydrate equilibrium data in the presence of ionic liquid. **At 30 Bar, the equilibrium temperature of methane hydrate was reduced from 1.52 °C to 1.30 °C** in the presence of 1 wt% of [BMIM]-Br.

Table 7: Methane hydrates equilibrium data in the presence of ionic liquid

Sample	Measured Pressure (Bar)	Equilibrium Temperature (°C)
1 wt% of [BMIM]-Br	28.54	1.30

4.1.2 Equilibrium temperature at 60 Bar.

The experiment was then conducted at 60 Bar. Table 8 shows the experiment condition at 60 Bar. In order to achieve 60 Bar pressure, the piston inside the sapphire cell was increased to compress the cell. The same sample of 1 wt% [BMIM]-Br was used for this run but the temperature set point was altered due to the changes in pressure. At 60 Bar, the equilibrium temperature of pure methane was noted at 8.41 °C [18].

Table 8: Experiment condition at 60 Bar

Sample	Pressure (Bar)	Pure Methane Equilibrium Temperature (°C)
1 wt% of [BMIM]-Br	60	8.41

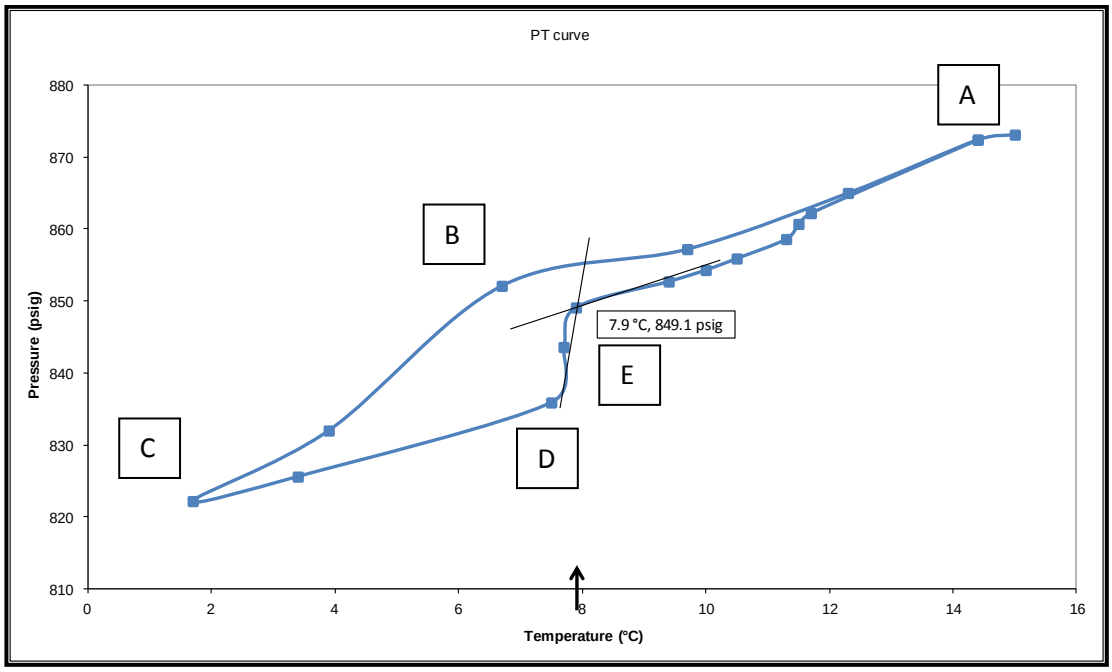


Figure 14: Pressure and temperature curve of methane hydrate at 60 Bar

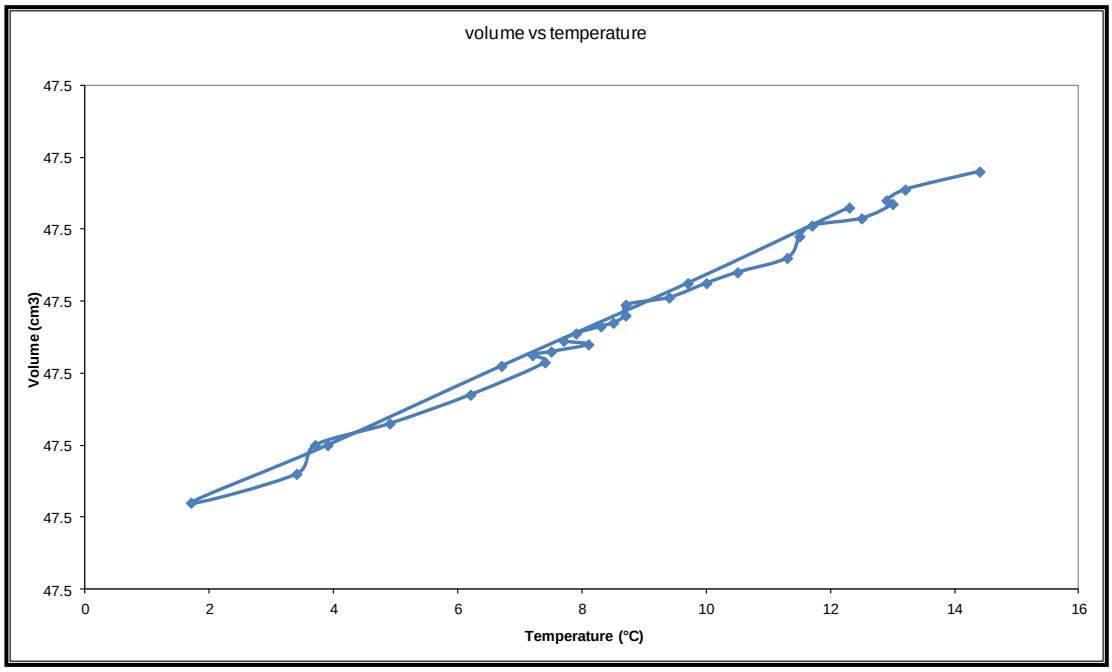


Figure 15: Volume and temperature curves at 60 Bar

Figure 14 shows the result of pressure and temperature curves of methane with 1 wt% of [BMIM]-Br. Similar trend can be seen from this curve. Compared to the previous run, the sudden pressure drop was noted earlier at 6.7 °C (point B). At this point the methane hydrate started to form. The formation of hydrate was observed above 0 °C and methane hydrate was fully formed at temperature of 1.7 °C (point C).

The similar trend was seen during the heating process. Pressure increased rapidly from point D to E reflecting the freed methane gas from the ice structure and methane hydrate started to dissociate. Line from point C to point D reflected the dissociation of the sample. **The intersection of two lines at point E shows the hydrate equilibrium temperature and pressure of the sample**. The equilibrium pressure was noted at 58.54 Bar and the equilibrium temperature was noted at 7.90 °C. At this point, methane hydrate has fully dissociated. Figure 15 shows the volume and temperature curves at 60 Bar. The volume was kept constant (isochoric) at about 48 cm^3. Table 9 summarizes the methane hydrate equilibrium data in the presence of ionic liquid. At 60 Bar, the **equilibrium temperature of methane hydrate was reduced from 8.41 °C to 7.91 °C** in the presence of 1 wt% of [BMIM]-Br**.**

Table 9: Methane hydrates equilibrium data in the presence of ionic liquid

Sample	Measured Pressure (Bar)	Equilibrium Temperature (°C)
1 wt% of [BMIM]-Br	58.54	7.91

4.2 HYDRATE EQUILIBRIUM CURVE COMPARISON

In this section, the measured data obtained from the first section was compared with other hydrate inhibitor equilibrium curve from past research. The result was compared to analyze the effectiveness of [BMIM]-Br with other type of hydrate inhibitor. Table 10 summarizes the measured data obtained from the experiment. Two equilibrium points were measured from the pressure temperature curves of methane hydrate in the presence of ionic liquid.

Table 10: Measured data 1 wt% [BMIM]-Br

Pressure (Bar)	Temperature (°C)
28.54	1.30
58.54	7.91

The measured data was plotted and compared with the phase equilibrium of pure methane [18], [EMIM]-Cl [16] **Error! Reference source not found.**and methanol [18]. Table 11 shows the past research data that was compared with the measure data.

Table 11: Past research data

Pressure (Bar)	Temperature (K)		
	Pure Methane	1 wt% [EMIM]-Cl	10 wt% Methanol
30	274.52		269.56
50	279.63	279.30	
60	281.4	280.78	276.37

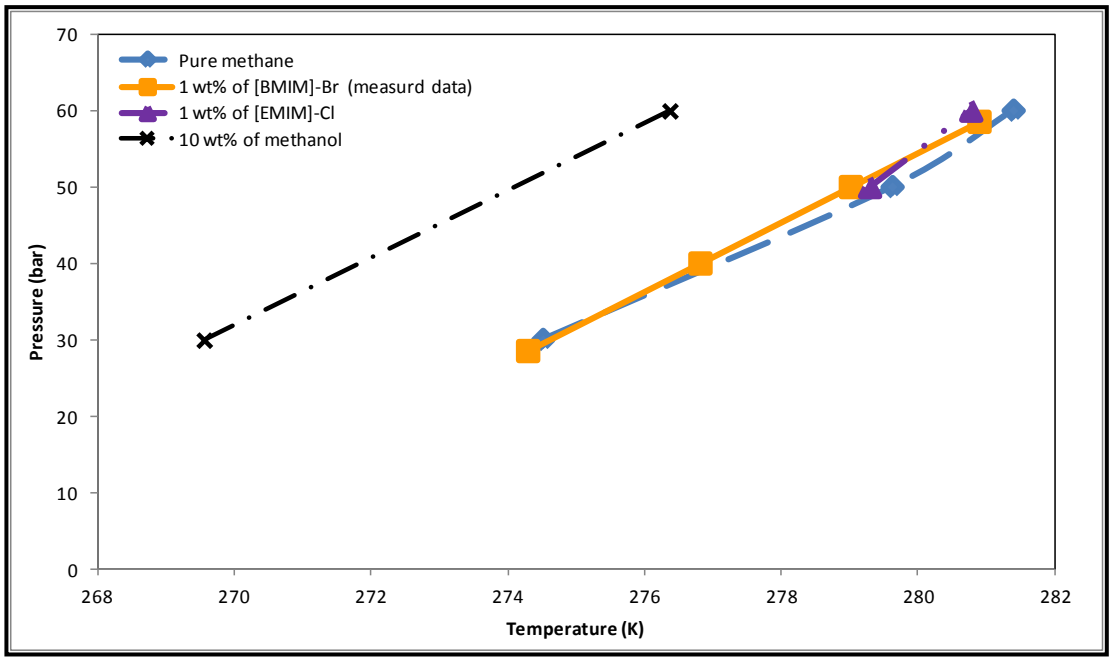


Figure 16: Phase boundary of methane hydrate in the presence of 1 wt% [EMIM]-Cl (B. Partoon et al., 2003), 1 wt% of [BMIM]-Br (measured data), 10 wt% of methanol (Ng and Robinson, 1986) and pure water (Nakamura et al., 2003)

Figure 16 compares the sample in the presence of 1 wt% of [BMIM]-Br (measured data) with other hydrate inhibitor from previous research. Methanol shifts the equilibrium temperature of methane hydrate the most compared to other hydrate inhibitor. However, 10 wt% of methanol was required to show a significant temperature shift. **The temperature shift of methane hydrate in the presence of ionic liquid is not significant due to the limited data obtained from the measurement.** The thermodynamic effect of [BMIM]-Br is not clear compared to the conventional hydrate inhibitor (methanol).

More data is needed to analyze the thermodynamic effect of ionic liquid towards the phase equilibrium of methane hydrate. However, there is insignificant temperature shift observed in the presence of 1 wt% [BMIM]-Br. At 30 Bar, the equilibrium temperature of methane hydrates shift from 1.52 °C to 1.30 °C whereby at 60 Bar, the equilibrium temperature shift from 8.41 °C to 7.91 °C.

Table 12: Temperature shift

Pressure (Bar)	Temperature (°C)		Δ T
	Pure methane	Sample	
30	1.52	1.32	0.2
60	8.41	7.91	0.5

Table 12 shows the temperature shift measured in the presence of 1 wt% of [BMIM]-Br. As the pressure increased from 30 Bar to 60 Bar, the temperature shift increased. This shows that thermodynamic effect of [BMIM]-Br increased at high pressure. Although the thermodynamic effect is not significant compare to methanol, **ionic liquid shows an increase of temperature shift at 60 Bar.** However, this is not conclusive since only two different range of pressure being tested. Further measurement need to be done to confirm the effectiveness of ionic liquid at higher pressure.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

As a conclusion, ionic liquid is investigated as hydrate inhibitor at different range of pressure and temperature. Although the thermodynamic effect of ionic liquid measured in this research is not significant due to the limited data, the thermodynamic effect of ionic liquid is observed since it shifts the equilibrium temperature of methane hydrate to a lower temperature. At 30 Bar, the equilibrium temperature of methane hydrates shift from 1.52 ℃ to 1.30 ℃ whereby at 60 Bar, the equilibrium temperature shift from 8.41 ℃ to 7.91 ℃. In comparison to conventional hydrate inhibitor, methanol shows a significant temperature shift about -3.44 ℃ from 1.52 ℃ (pure methane) at 30 Bar. However, methanol is known as high dosage hydrate inhibitor and harmful to the environment. From this research, [BMIM]-Br shift the temperature more at 60 Bar compared to 30 Bar which shows that thermodynamic effect of ionic liquid increase at higher pressure.

5.2 RECOMMENDATIONS

To improve the results from this research, the author have few recommendations. The samples need to be tested at different range of pressure ranging about 20 Bar to 80 Bar to observe a clear performance of ionic liquid. Several concentrations of ionic liquid can be done to observe the concentration effect of ionic liquid towards the equilibrium phase of methane hydrate. Hence, the optimum concentration of ionic liquid can be measured.

Sample preparation is also important. The samples need to be prepared within 24 hours to get more accurate data. If the samples are left too long, the composition of the ionic liquid and water may be affected. Experiment on the effectiveness of ionic liquid prepared at different time range can be done to investigate the effect of time for sample preparation towards the effectiveness of ionic liquid. For this experiment, the sample is prepared 24 hours before the experiment was conducted.

Due to the material limitation, distilled water was used in this research. During the sample preparation, distilled water was mixed with ionic liquid powder. However, deionized water is more preferable to study the formation and the dissociation methane hydrate instead of distilled water to get accurate data.

The temperature set point is one of the important data need to be input at HYDREVAL software. If the temperature set point is incorrect, the result may be affected. Thus, in order to measure the temperature set point, modeling need can be done. From the modeling, expected equilibrium temperature of methane hydrate can be measured.

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